(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 002 889 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.05.2000 Bulletin 2000/21

(51) Int. Cl.[7]: **C23C 22/68**, B05D 3/10, B05D 7/14, C09D 5/08

(21) Application number: **99123109.3**

(22) Date of filing: **18.11.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **18.11.1998 JP 32804098**

(71) Applicant:
Nippon Paint Co., Ltd.
Osaka-shi Osaka-fu (JP)

(72) Inventors:
- **Shimakura, Toshiaki**
  Ichikawa-shi, Chiba-ken (JP)
- **Yamasoe, Katsuyoshi**
  Sakura-shi, Chiba-ken (JP)

(74) Representative: **HOFFMANN - EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) Anti-corrosive coating compositions and methods for metal materials

(57) The present invention provides an anti-corrosive coating composition suitable for metal, particularly zinc-coated steel plates, which is free of chromium, is capable of conferring excellent corrosion resistance on the metal coated therewith, and is excellent in storage stability, in which silane coupling agent and/or hydrolyzate condensates thereof is contained in water or an aqueous resin solution or suspension; in addition the composition may additionally contain phosphorus containing ions and/or sulfur-containing compound or sulfur-containing ions; a method for anti-corrosive coating of metal materials and metal materials coated with the composition.

EP 1 002 889 A2

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to an anti-corrosive coating composition for metal materials particularly zinc-coated steel plates or non-coated steel, a method for anti-corrosive treatment using it, and metal materials subjected to the anti-corrosive treatment.

[0002] Conventionally, chromate-based surface-treating agents for chromate treatment or chromate phosphate treatment are used in anti-corrosively treating compositions for metal and widely used even now. However, in view of a trend toward environmental regulation in recent years, there is the possibility that their use may be limited in the future due to the toxicity particularly carcinogenesis of chromium. Hence, there was a need for development for a chromium-free, anti-corrosively treating composition having equivalent corrosion resistance to that of chromium. As described in Japanese Patent Application No. Hei. 10-36264, the present inventors developed a non-chromium, anti-corrosively treating composition containing a thiocarbonyl group-containing compound, phosphate ions and further water-dispersable silica in an aqueous resin. However, this system was regretfully insufficient in storage stability and there was a problem with corrosion resistance in the case of thin film. On one hand, with respect to silane coupling agents, there is an acidic surface-treating agent containing two kinds of silane coupling agents as disclosed in JP-KOKAI Hei. 8-73775, but this is a system utilized to improve fingerprint resistance and coating adhesion, and its corrosion resistance is not satisfactory for the purpose of achieving high corrosion resistance as required in the present invention after coating of an anti-corrosively treating composition. Further, JP-KOKAI Hei. 10-60315 discloses a surface treating agent for steel structures which comprises a silane coupling agent having a specific functional group reacting with an aqueous emulsion, but the corrosion resistance required in this prior art is against a relatively mild test such as wetting test, which is in comparable to the corrosion resistance of the anti-corrosively treating composition in the present invention which as thin film, is durable in a severe anti-corrosion test such as saline spray test. From the foregoing, there was a need for the development of a non-chromium, anti-corrosively treating composition which exhibits corrosion resistance for thin film.

SUMMARY OF THE INVENTION

[0003] The present invention provides an anti-corrosive coating composition suitable for metal, particularly zinc-coated steel plates, which is free of chromium, is capable of conferring excellent corrosion resistance on a metal coated therewith, and is excellent in storage stability.

[0004] The first embodiment of the present invention relates to an anti-corrosive coating composition comprising a silane coupling agent and/or hydrolyzate condensates thereof in water in an amount of 0.1 to 50 g per one liter of the composition.

[0005] The second embodiment of an anti-corrosive coating composition of the present invention comprises in addition to the first embodiment of the composition at least one kind of phosphorus-containing ions in an amount of 0.1 to 100 g/l and/or at least one kind of sulfur-containing compound or sulfur-containing ions in an amount of 0.1 to 100 g/l.

[0006] The third embodiment of the present invention relates to an anti-corrosive coating composition comprising a silane coupling agent and/or hydrolyzate condensates thereof in an amount of 0.1 to 50 g/l in one liter of an aqueous resin solution or an aqueous resin suspension.

[0007] The fourth embodiment of an anti-corrosive coating composition of the present invention comprises in addition to the third embodiment, at least one kind of phosphorus-containing ions in an amount of 0.1 to 5 g/l, and/or at least one kind of sulfur-containing compound or sulfur-containing ions in an amount of 0.1 to 50 g/l.

[0008] In addition, the present invention relates to a method for anti-corrosive coating of metal materials, which comprises coating metal materials with the anti-corrosive coating composition described above.

[0009] Further, the present invention relates to a method for anti-corrosive coating of metal materials, which comprises coating metal materials with the resin-free, anti-corrosive coating composition described above, then drying and coating it with an anti-corrosive coating composition containing at least an aqueous resin solution or an aqueous resin suspension and a silane coupling agent.

[0010] Furthermore, the present invention relates to an anti-corrosively treated metal material comprising metal materials coated with any one of the anti-corrosive coating compositions deecribed above.

[0011] In addition, the present invention relates to an anti-corrosively treated metal material comprising metal materials coated by any one of the anti-corrosive-coating methods described above.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention relates to an anti-corrosive coating composition comprising a silane coupling agent

Table 5

		primary anti-corrosive properties humidity		topcoat adhesion properties	
		SST	resistance	primary	secondary
Example	32	9	10	10	10
	33	10	10	10	10
	34	10	10	10	10
	35	10	10	10	10
	36	10	10	10	10
	37	10	10	10	10
	38	9	10	10	10
Comparative Example	8	1	1	4	2
	9	1	2	8	6

Comparative Example 6 and 7

[0083] The steel plate whose substrate for coating was treated with the treating agents used in Comparative Examples 4 and 5 in the same manner as in Comparative Examples 4 and 5 as well as the coated steel plate on which the topcoat was applied were evalulated for its primary anti-corrosive properties and topcoating adhesion properties in the same manner as in Examples 25 to 31. The results along with those of Examples 25 to 31 are shown in Table 3.

Comparative Examples 8 and 9

[0084] The steel plate whose substrate for coating was treated with the treating agents used in Comparative Examples 4 and 5 in the same manner as in Comparative Examples 4 and 5 as well as the coated steel plate on which the topcoat was applied were evaluated for its primary anti-corrosive properties and topcoating adhesion properties in the same manner as in Examples 32 to 38. The results along with those of Examples 32 to 38 are shown in Table 5.

[0085] By applying the non-chromium type anti-corrosive coating composition of the present invention, galvanized steel plates can be endowed with corrosion resistance superior to that of conventional chromate-containing anti-corrosively treating composition. Further, it was confirmed that the anti-corrosive coating composition of the present invention is also excellent in storage stability.

Claims

1. An anti-corrosive coating composition comprising a silane coupling agent and/or hydrolyzate condensates thereof in water in an amount of 0.1 to 50 g per one liter of the composition.

2. An anti-corrosive coating composition comprising a silane coupling agent and/or hydrolyzate condensates thereof and at least one kind of phosphorus-containing ions selected from the group consisting of phosphate ions, phosphite ions and hypophosphite ions in water in an amount of 0.1 to 50g and 0.1 to 100 g per one liter of the composition respectively.

3. An anti-corrosive coating composition comprising a silane coupling agent and/or hydrolyzate condensates thereof and at least one kind of sulfur-containing compound or sulfur-containing ions selected from the group consisting of thiocarbonyl compounds, triazine thiol compounds, sulfide ions, persulfate ions and thiosulfate ions in water in an amount of 0.1 to 50g and 0.1 to 100 g per one liter of the composition respectively.

4. An anti-corrosive coating composition comprising a silane coupling agent and/or hydrolyzate condensates thereof, at least one kind of phosphorus-containing ions selected from the group consisting of phosphate ions, phosphite ions and hypophosphite ions, and at least one kind of sulfur-containing compound or sulfur-containing ions selected from the group consisting of thiocarbonyl compounds, triazine thiol compounds, sulfide ions, persulfate